On the Single-Line Spectra of Magnesium and other Metals and their Ionising Potentials.

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[Plate 2.]

1. *Introduction.*

It has been shown by Frank and Hertz* that when heated mercury vapour is traversed by electrons possessing kinetic energy slightly above that acquired in a fall of potential of 4·9 volts the vapour is stimulated to the emission of the single spectral line $\lambda = 2536{\cdot}72$ Å.U. It has also been shown by McLennan and Henderson† that a spectrum consisting of this single line only can be obtained from mercury vapour when it is bombarded by electrons possessing energy corresponding to any fall of potential within a range beginning at about 5 volts and extending up to slightly over 10 volts. The investigation has also been extended by McLennan and Henderson to include a study of the radiation emitted by zinc and cadmium vapours when traversed by electrons. With these vapours they have found that single-line spectra can be obtained when the electrons traversing these vapours possess kinetic energy lying within a limited and clearly defined range, which has not been fully investigated as yet but which corresponds roughly to potential differences lying between 4 volts and 13·6 volts. With zinc vapour the single-line spectrum consists of light of wave-length $\lambda = 3075{\cdot}99$ Å.U., and with cadmium vapour of light of wave-length $\lambda = 3260{\cdot}17$ Å.U. It should be pointed out here that the lines $\lambda = 2536{\cdot}72$ Å.U., $\lambda = 3075{\cdot}99$ Å.U., and $\lambda = 3260{\cdot}17$ Å.U. are respectively the first members of Paschen's‡ combination series $\nu = 2, p_2 - m$, S, for the elements mercury, zinc and cadmium.

2. *The Single-Line Spectrum of Magnesium.*

Since the publication of the results described above, the radiation from magnesium vapour traversed by electrons has been investigated by the writer and it has been found with this element, too, that a single-line spectrum can be obtained if the electrons bombarding the vapour possess energy lying within a certain range, whose limits also have not as yet been definitely

* 'Verh. d. Deutsch. Phys. Ges.,' vol. 11, p. 512 (1914).

† 'Roy. Soc. Proc.,' A, vol. 91, p. 485 (1915).

‡ Paschen, 'Ann. der Phys.,' vol. 35, p. 860 (1911).

determined but which covers a portion at least of the ranges mentioned above for mercury, zinc, and cadmium. In carrying out these experiments the apparatus used and the procedure followed was precisely the same as that described in the paper by McLennan and Henderson. With magnesium the single-line spectrum consists of light of wave-length $\lambda = 2852{\cdot}22$ Å.U. The ordinary spark spectrum of magnesium in air is shown in the upper row in Plate 2, fig. 1, and the single-line spectrum of the vapour of the metal in the second row of the same figure. The latter was obtained with a three-hour exposure, and the electrons which stimulated the vapour to the emission of this radiation acquired their kinetic energy with an arcing potential of 8·2 volts applied between the Wehnelt cathode and the positive terminal.

3. *The Absorption Spectra of Magnesium and other Metallic Vapours.*

In a paper recently published by McLennan and Edwards* it has been shown that in the absorption spectrum of mercury there is an absorption band at $\lambda = 2536{\cdot}72$ A.U. and one at $\lambda = 1849{\cdot}6$ Å.U. With this vapour it has been found that there is also a complex band obtainable at $\lambda = 2338$ Å.U. when high vapour densities are used. With zinc and cadmium vapours it has been shown by the same writers that the absorption spectra consist of but two absorption bands. With zinc vapour these are at $\lambda = 3075{\cdot}99$ Å.U. and at $\lambda = 2139{\cdot}3$ Å.U., and with cadmium vapour they are at $\lambda = 3260{\cdot}17$ A.U. and at $\lambda = 2288{\cdot}79$ Å.U. As pointed out above, the lines $\lambda = 2536{\cdot}72$ Å.U., $\lambda = 3075{\cdot}99$ Å.U. and $\lambda = 3260{\cdot}17$ Å.U. are the first members of Paschen's combination series for the three elements represented by $\nu = 2, p_2 - m$, S, and they are therefore the lines of this series corresponding to the value $m = 1{\cdot}5$. Again, it will be seen by referring to Paschen's† paper that the lines $\lambda = 1849{\cdot}6$ Å.U., $\lambda = 2139{\cdot}13$ Å.U. and $\lambda = 2288{\cdot}79$ Å.U. are the first members of the series $\nu = 1{\cdot}5$, $\mathrm{S} - m$, P, predicted by Paschen and later identified by Wolff‡ for the three elements mercury, zinc, and cadmium.

It does not appear from communications which have come to the notice of the writer that a series of lines corresponding to $\nu = 1{\cdot}5$, $\mathrm{S} - m$, P, has as yet been identified in the spectrum of magnesium, but if we assume that the line $\lambda = 2852{\cdot}22$ Å.U. is the first line in the combination series $\nu_1 = 2, p_2 - m$, S, for this element sufficient information is given in a paper by Dunz§ to cal-

* McLennan and Edwards, 'Proc. Roy. Soc. of Canada,' 1915; 'Phil. Mag.,' November, 1915.

† Paschen, *loc. cit.*

‡ Wolff, 'Ann. der Phys.,' vol. 42, p. 525 (1913).

§ Dunz, 'Bearbeitung unserer Kenntnisse von den Serien,' Inaug. Diss., Tübingen, 1911.

culate the first and the last member of the series $\nu = 1 \cdot 5$, S$-m$, P, for this metal. In the paper by Dunz referred to the frequency of $\nu = 2$, p_2, in the magnesium spectrum is given as 39793·21. If we take the frequency of the line $\lambda = 2852 \cdot 22$ Å.U. to be 35050·45 it follows that the frequency $\nu = 1 \cdot 5$, S, is equal to 74843·66. This will then be the frequency of the last line of the series spectrum of magnesium given by $\nu = 1 \cdot 5$, S$-m$, P. Again, in the paper by Dunz the frequency $\nu = 2$, P, is given as 26612·7 and from this it follows that the frequency of the first line in the series $\nu = 1 \cdot 5$, S$-m$, P, *i.e.* $\nu = 1 \cdot 5$, S-2, P, is 48230·96. This it will be seen is the frequency of the line $\lambda = 2073 \cdot 36$ Å.U. If then the vapour of magnesium behaves as regards absorption in a manner analogous to the vapours of mercury, zinc, and cadmium, the absorption spectrum of magnesium vapour should contain absorption bands at $\lambda = 2852 \cdot 22$ Å.U. and at $\lambda = 2073 \cdot 36$ Å.U. On looking up the literature on the subject it was found that Wood and Guthrie,* and Eder and Valenta,† had already shown that there is an absorption band in this spectrum at $\lambda = 2852 \cdot 22$ Å.U., but as no one seemed to have found any band at $\lambda = 2073 \cdot 36$ Å.U. some experiments were made to see if it really existed. The experiments confirmed its existence and a reproduction of one of the photographs taken is shown in fig. 2. The upper portion of this figure was taken with the light from the spark between magnesium terminals in air and the lower one with the same light after it had traversed an evacuated clear fused quartz tube containing heated non-luminous magnesium vapour. As the reproduction shows, absorption occurred at $\lambda = 2852 \cdot 22$ Å.U. and at $\lambda = 2073 \cdot 36$ Å.U. as well. In addition a narrow absorption band appears at $\lambda = 2536 \cdot 72$ Å.U. This band also appeared in the experiments of McLennan and Edwards referred to above in the absorption spectrum of zinc and cadmium vapours, and it was no doubt due to a trace of mercury vapour which may have come from mercury originally present as an impurity in the metals or from mercury which got into the absorption tubes containing the vapour when these tubes were exhausted by the Gaede mercury pump. From this result it will be seen that the absorption spectrum of magnesium vapour is exactly analogous to the absorption spectrum of mercury, zinc, and cadmium. The analogy, moreover, between the absorption spectrum of magnesium and that of mercury is more perfect than would appear from the above considerations, for the absorption band at $\lambda = 2536 \cdot 72$ Å.U. in the absorption spectrum of mercury vapour comes out with small vapour densities as two narrow absorption bands whose wave-lengths have been given by

* Wood and Guthrie, 'Astrophys. Journ.,' vol. 29, No. 1, p. 211 (1909).

† Eder and Valenta, 'Atlas Typischer Spectren,' Table XXVII.

R. W. Wood* as $\lambda = 2536$ Å.U., and $\lambda = 2539$ Å.U. The absorption band at $\lambda = 2852{\cdot}22$ Å.U. in the absorption spectrum of magnesium vapour has also been found to consist of two narrow sharply defined bands very close together. These are shown in the reproduction in fig. 3, which was obtained by greatly enlarging the band shown in fig. 2, at $\lambda = 2852{\cdot}22$ Å.U. The bands at $\lambda = 3075{\cdot}99$ Å.U., and $\lambda = 3260{\cdot}17$ Å.U., in the absorption spectra of zinc and cadmium vapours have not as yet been resolved into analogous doublets.

4. *The Ionising Potentials of Different Elements.*

In the paper by McLennan and Henderson mentioned above attention was drawn to a paper by Frank and Hertz† which described experiments leading to the conclusion that the minimum energy required to ionise an atom of mercury was that acquired by an electron in passing through a fall of potential of 4·9 volts. Attention was also drawn in this paper to a second communication by Frank and Hertz,‡ in which it was shown that in the quantum relation $Ve = h\nu$, where $V = 6{\cdot}6 \times 10^{-27}$ erg sec., 4·9 volts is the potential fall which corresponds to the frequency of the line $\lambda = 2536{\cdot}72$ Å.U. From this it follows that for mercury atoms at least a knowledge of the wave-length of the single-line spectrum of this element is sufficient to enable one to calculate the ionising potential. If the relation just pointed out be applicable generally to all the elements it follows that if the vapour of an element can be shown to be capable of exhibiting a single-line spectrum the frequency of this single spectral line may be used to deduce the minimum amount of energy required to ionise the atoms of that element. From the considerations already presented in this paper it will be seen that the wave-lengths of the single spectral lines in the single-line spectra of the elements have the frequencies given by $\nu = 2, p_2 - 1{\cdot}5, S$, and as these frequencies are now known for mercury, zinc, cadmium, and magnesium, it follows that if Frank and Hertz have put the correct interpretation upon their experiments —and it may be added here that their experiments have apparently been confirmed quite recently by Newman§—then the ionising potentials for the atoms of all these elements can be calculated by the relation $Ve = h\nu$. The results of this calculation are given in Table I.

In the paper by McLennan and Henderson it was pointed out that in order to obtain the single-line spectra with mercury, zinc and cadmium vapours, it was necessary that the electrons bombarding these vapours should not

* R. W. Wood, 'Astrophys. Journ.,' vol. 26, No. 1, p. 41.

† Frank and Hertz, 'Verh. d. Deutsch. Phys. Ges.,' vol. 10, pp. 457–467.

‡ Frank and Hertz, 'Verh. d. Deutsch. Phys. Ges.,' vol. 11, p. 512.

§ Newman, 'Phil. Mag.,' vol. 28, pp. 753–756 (November, 1914).

Table I.

Element.	Wave-length with frequency $\nu = 2, p_2 - 1{\cdot}5, S$.	Ionising potential calculated on bases of conclusions of Frank and Hertz.
	Å.U.	volts.
Mercury	2536·72	4·9
Zinc	3075·99	3·96
Cadmium	3260·17	3·74
Magnesium	2852·22	4·28

possess kinetic energy greater than that acquired in passing through falls of potential of 12·5, 11·8, and 15·3 volts respectively for the three vapours. If the electrons possessed kinetic energy greater than that given by these voltages visible arcs were struck and the many-lined spectra were obtained for the three elements. In the paper mentioned it was also stated that as these voltages gave with the relation $Ve = h\nu$, approximately the wave-lengths of the limiting lines in the series $\nu = 1{\cdot}5, S - m, P$, for the three elements, the results might be interpreted as indicating possibly a second type of ionisation which the atoms of these elements might be capable of undergoing. If this interpretation should turn out to be correct it would follow, since the frequencies of the limiting lines in the series $\nu = 1{\cdot}5, S - m, P$, are given by $\nu = 1{\cdot}5, S$, that the ionising potentials of the second type are given by $V = h(1{\cdot}5, S)/e$. Applying this relation to the results already obtained and given above, the ionising potentials of the second type have been calculated for mercury, zinc, cadmium, and magnesium, and are given below in Table II.

Table II.

Element.	Wave-lengths corresponding to frequency $\nu = 1{\cdot}5, S$.	Ionising potentials calculated from $V = h(1{\cdot}5, S)/e$.
	Å.U.	volts.
Mercury	1188·0	10·27
Zinc	1320·0	9·24
Cadmium	1378·7	8·85
Magnesium	1336·1	9·13

5. *Ionising Potentials and Bohr's Theory of the Origin of Radiation.*

In the theory which has been brought forward by Bohr,* the atom of an element is supposed to consist of a positive Rutherford nucleus surrounded

* Bohr, 'Phil. Mag.,' vol. 26, pp. 1, 476, 857 (1913); vol. 27, p. 506 (1914); and vol. 30, p. 394 (1915).

by one or more rings of electrons, revolving in stationary or non-radiating orbits about the nucleus. In the neutral or most stable state the electrons are revolving in the orbits of smallest possible area. The diagram in fig. 4 may be taken to illustrate this point.

A neutral atom may be supposed, for example, to consist of a positive nucleus E surrounded by two rings of revolving electrons A and B. If

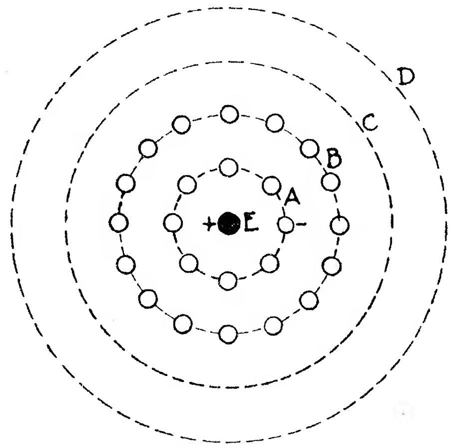


Fig. 4.

through some agency such as an electronic bombardment, one or more of the electrons in the ring B be made to revolve in the orbit C, then, according to the theory of Bohr, these electrons would not radiate while revolving in the orbit C, but they would send out a radiation of a single determinate wave-length in passing back from the orbit C to the stable orbit B. Extending the theory still further, if the disturbing agency caused one or more of the electrons in the orbit B to revolve in the orbit D, then, as the electrons might drop back either directly to the orbit B or to the orbit C first and then to the orbit B, it would appear that an atom subjected to such a disturbance would be capable in returning to the neutral state of emitting a radiation consisting of two, and possibly three, definite and determinate wave-lengths. It would then seem from Bohr's theory that atoms of a vapour bombarded by electrons should be capable of emitting either a single-line spectrum, a two- or three-line spectrum, a three- or six-line spectrum, etc., according to the violence of the shock to which it was subjected.

Again, according to the theory of Bohr, ionisation of an atom could only be said to have taken place when the disturbing agency caused one or more electrons to be projected out from the electronic system beyond the outermost stationary or non-radiating orbit of the atom. This theory would

therefore predicate but one type of ionisation for atoms. By applying the theory to the matters discussed in the present communication, it would appear that atoms in the state to emit a single-line spectrum could not be said to be ionised. It would follow, then, that if Bohr's theory of the origin of radiation be correct, the interpretation placed by Frank and Hertz on the results of their direct investigation of the ionising potentials for mercury atoms cannot be the correct one. On the other hand, in the experiments of Henderson and myself, in which the single-line spectra were obtained with mercury, zinc, cadmium, and magnesium vapours when they were bombarded by electrons, the fields in which these bombarding electrons acquired their energy covered a range of from about 5 volts to slightly over 10 volts. It is probable that, under these conditions, the great majority of the bombarding electrons would acquire just sufficient energy to stimulate the atoms of the vapours traversed to the emission of a radiation of but a single wave-length. The second absorption bands, however, in the absorption spectra of mercury, zinc, cadmium, and magnesium vapours, it will be recalled, come at $\lambda = 1849{\cdot}6$ Å.U., $\lambda = 2139{\cdot}3$ Å.U., $\lambda = 2288{\cdot}79$ Å.U., and $\lambda = 2073{\cdot}36$ Å.U. respectively, and it will be seen, therefore, that if the quantum relation $Ve = h\nu$ be applicable, the potential falls corresponding to these wave-lengths are well within the range extending from 5 to 10 volts. One would have expected, therefore, that with arcing potentials of 10 volts, one should have found traces, at least, of the lines $\lambda = 1849{\cdot}6$ Å.U., $\lambda = 2139{\cdot}3$ Å.U., $\lambda = 2288{\cdot}79$ Å.U., and $\lambda = 2073{\cdot}36$ Å.U., accompanying the lines $\lambda = 2536{\cdot}72$ Å.U., $\lambda = 3075{\cdot}99$ Å.U., $\lambda = 3260{\cdot}17$ Å.U., and $\lambda = 2852{\cdot}22$ Å.U., in the spectra emitted by the three vapours. No indication of these lines, however, was found in any of the experiments of Henderson and myself, even with exposures of five hours' duration, and with vapours covering a wide range of densities. It should be remembered, however, that even if some of the atoms of the vapours traversed were stimulated to the emission of the shorter wave-lengths mentioned, the radiation of these wave-lengths might have been absorbed in passing through the outer layers of the vapour in the arcing tube. The experiments of Henderson and myself cannot, therefore, be taken as being opposed to the correctness of Bohr's theory. If, however, this theory be correct, then it does follow that Frank and Hertz have incorrectly interpreted their results. Moreover, if it should turn out that they, and also Newman, have placed the wrong interpretation on the results of their investigations, then the ionising potentials for mercury, zinc, cadmium, and magnesium would not be those given in Table I, but they would in all probability be those given in Table II, and we would therefore arrive at the conclusion that there is but one type of ionisation for atoms.

6. *Summary of Results.*

1. It has been shown that magnesium vapour traversed by electrons can be stimulated to the emission of a single-line spectrum consisting of the wave-length $\lambda = 2852{\cdot}22$ Å.U.

2. It has been shown that the absorption spectrum of non-luminous magnesium vapour contains an absorption band at $\lambda = 2852{\cdot}22$ Å.U., and one at $\lambda = 2073{\cdot}36$ Å.U.

3. As the lines $\lambda = 2852{\cdot}22$ Å.U., and $\lambda = 2073{\cdot}36$ Å.U., are respectively the first members of the series $\nu = 2, p_2 - m$, S, and $\nu = 1{\cdot}5$, S $- m$, P, respectively, the absorption spectrum of magnesium vapour has been shown to be analogous to the absorption spectra of the vapour of mercury, zinc, and cadmium.

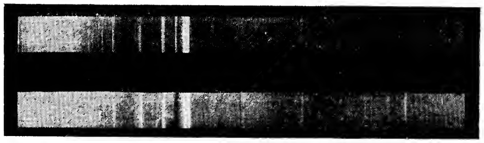
4. The ionising potentials have been deduced for atoms of magnesium, in addition to those for the atoms of mercury, zinc, and cadmium.

5. Considerations have also been presented which show that if Bohr's theory affords an explanation of the origin of single-line spectra, then Frank and Hertz and also Newman must have placed a wrong interpretation on the results of their direct investigation of the ionising potentials for mercury atoms.

In conclusion the writer wishes to acknowledge his indebtedness to his assistant, Mr. P. Blackman, for his help in connection with the photographic work of the present investigation.

2852·22 Å.U.

Fig. 1.



2852·22 Å.U. 2536·72 Å.U. 2073·36 Å.U.

Fig. 2.

2852·22 Å.U.

Fig. 3.

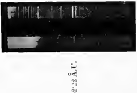


FIG. 1.

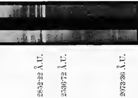


FIG. 2.

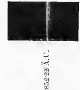


FIG. 3.